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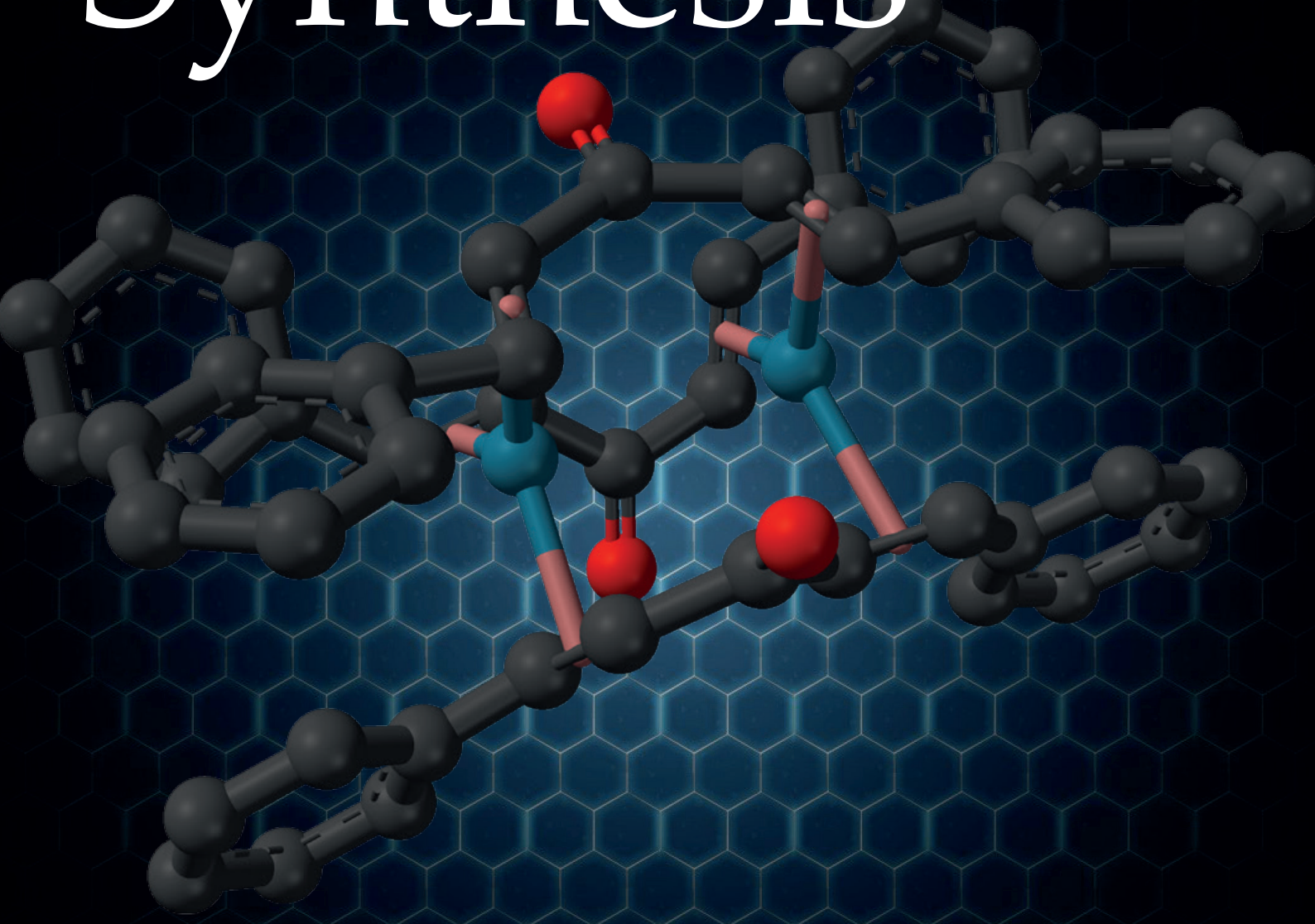

Mini Review

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Tris(dibenzylideneacetone)dipalladium: New Life of the Old Synthon for Pd(0) atom

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Tris(dibenzylideneacetone)dipalladium: New Life of the Old Synthon for Pd(0) atom

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Abstract: The history of a unique stable and soluble complex $Pd_2(dba)_3$ has been considered starting with the classical oxidative addition and finishing by the modern synthesis of Pd nanoclusters catalysts absorbed on the carbon and non-carbon polymer supports. Coordinatively non-saturated Pd(0) particles are used for constructing nanopalladium clusters immobilised which are active as catalysts in the cross-coupling reactions.

Keywords: *Fullerenes; Nanodiamonds; Graphenes; Tungsten-Disulphides Nanotubes; Heterogeneous Catalysts; Cross-Coupling Reactions*.

1. INTRODUCTION

It is well-known nowadays that many transition metals are able to form complexes in which the central metal atom is surrounded with neutral ligands keeping the formal valence equal to zero. Due to the intramolecular charge transfer the real charge (that can be calculated by quantum chemical methods) may differ from zero, being $(0 \pm \varkappa)$, where $\varkappa << 1$. The story of the zerovalent complexes of noble metals began in the middle of last century with platinum and palladium.

The novel class of zerovalent complexes of platinum (with isonitriles as ligands) was discovered by Malatesta and Angoletta in mid-1950s [1]. The similar palladium complex was obtained later [2]. After it was found that tertiary phosphines and some diolefines, for example, cyclic dienes (like 1,5-cyclooctadiene) can also serve as ligands in the stable complexes of Pd(0) and Pt(0) [3]. In 1970 Ishii et al. [4] synthesized a new complex of Pd(0) with dibenzylideneacetone (dba) as a ligand. The product was obtained on reduction of $PdCl_2$ in methanol in the presence of the ligand as a mixture of complexes with different ratio of the components. Crystallization from an appropriate solvent (chloroform or benzene) afforded the well-defined solvate $Pd_2(dba)_3$*solv, 1 [5]. Unlike many other Pd(0) olefin complexes, compound 1 appeared to be surprisingly stable in air as a solid and in solution being at the same time apt to the easy ligand exchange. X-Ray investigation [6] revealed that the metal atoms are ligated through with the C=C bonds whereas the conjugated CO groups are not bound with metal (Fig. 1).

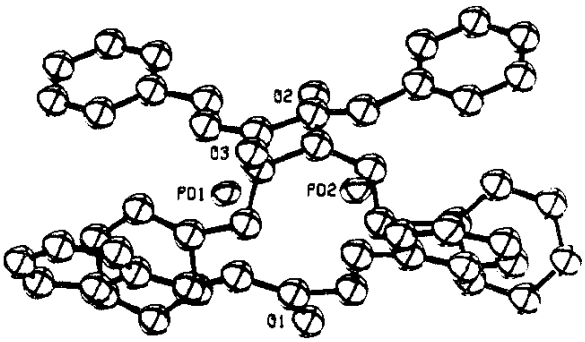


Figure 1. Diveric view of the $Pd_2(dba)_3$ molecule

Their role is probably in the increase of the stability of 1 due to the electron-withdrawing effect. In the most stable form, $Pd_2(dba)_3$, one metal atom is connected to three double bonds. Ligand dba in 1 is readily exchanged for tertiary phosphine, phosphate , or isonitrile:

$$Pd_2(dba)_3 + 8L = 2PdL_4 + 3dba$$
$$L = R_3P;\ (RO)_3P;\ RN{\equiv}C$$

Similar platinum analog was also prepared [7] but the synthesis gave the poorer yield, decomposed in part, and this complex did not get such a broad application as the palladium derivative. In recent years, the interest to $Pd_2(dba)_3$ as a source of Pd(0) aroused in the connection with the development of nanochemistry.

Professor Viacheslav I. Sokolov is the head of the Laboratory of Organometallic Stereochemistry in the Institute of Organoelement Compounds Russian Academy of Sciences in Moscow. He has graduated from Chemistry Department of Moscow University. During his scientific career he has published around 400 papers in peer-reviewed journals in organic, organometallic, or inorganic chemistry. For 20 years he was been a Member of the Editorial board of the Journal of Organometallic Chemistry.

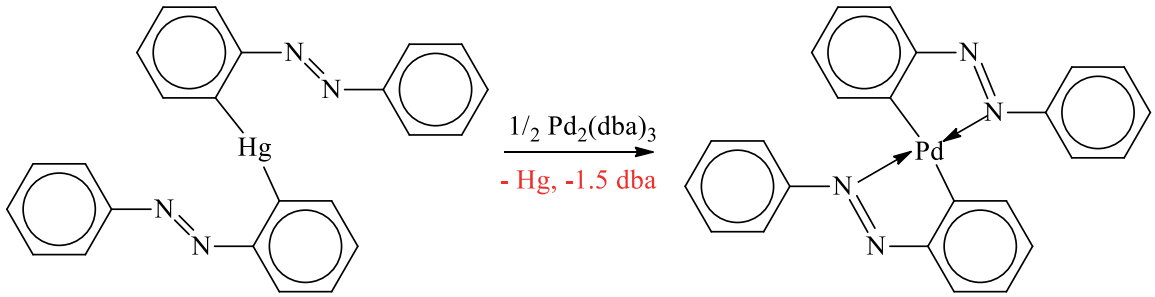
Dr. Natalya V. Abramova graduated from the Moscow Institute of Fine Chemical Technology. She has been postgraduate student and got PhD degree in the Institute of Organoelement Compounds Russian Academy of Sciences in Moscow. At present she is working in the area of nanocarbon including chemistry of fullerenes, carbon nanotubes, and related objects. She is investigating the novel method of preparing heterogeneous nanopalladium catalysts for the carbon-coupling reactions.

The novel class of zerovalent complexes of platinum (with isonitriles as ligans the dissociative mechanism of catalysis involving Pd(II) – Pd(0) system. The associative mechanism based on Pd(II) – Pd(IV) pair was also proposed [14] but less accepted. In many reactions with palladium salts, Pd black is formed that is complex or cluster of Pd(0) or Pd(I). Leonard and Franzen [15] observed the formation of hexagonal microstructures of 1 without admixture of metallic palladium.

Coordinatively unsaturated, Pd(0) species, can be considered as the electron-rich carbenoids, so they are apt to insert, for example, into some polyfluorinated molecules between two metalse 6) [21].

2. CLASSICAL PERIOD: REACTIONS OF OXIDATIVE ADDITION

The natural type of reactions for Pd(0) is certainly oxidative addition with organic halides and with the simultaneous conversation of Pd(0) to Pd(II). However, the loss of the loosely bonded ligand dba requires filling the vacant place with something else. The best choice is the intramolecular coordination with some donor atom such as nitrogen, sulfur etc. As a result, the product formed has a cyclic structure of the appropriate size, mostly five- or six-membered ring, rarely four- or seven-membered [8]. The extension of this approach for organomercurials has been the reaction of redox-demercuration [9] in which all Pd(0) and Pt(0) complexes can take part. This reaction shed light on the peculiar role of $Pd_2(dba)_3$ which donates to the product only the metal atom because of the special property of its loosely bonded ligand. Its role as a synthon for the single Pd(0) atom was clearly recognized and stressed in our early papers [10, 11] wherein the exchange of mercury atom for palladium was performed in the synthesis of the bis-chelated azoarene complexes (Scheme 1). Herein, it acts as a "conserved" Pd(0) atom very much like zinc liberating copper from its salts. The same approach was applied to the synthesis of a similar platinum derivative in the ferrocene series [12]. One can also note the application of the Pd(0) reagent in the stereochemical study of redox-demercuration [13].



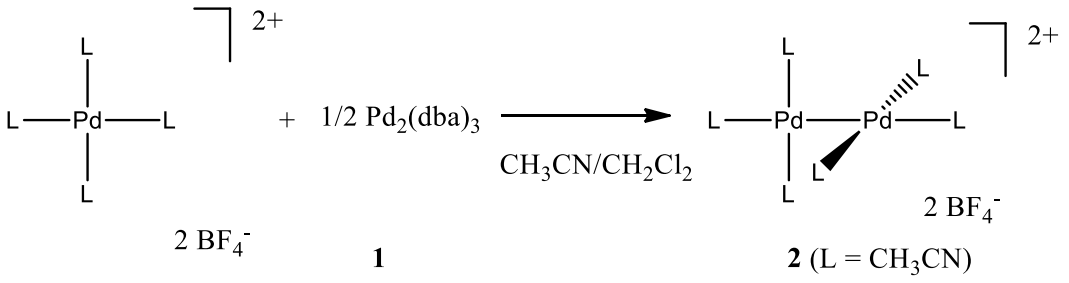
Scheme 1

3. $Pd_2(DBA)_3$ IN THE SYNTHESIS OF DI- AND POLYMETALLIC STRUCTURES

Palladium is one of the usable metals in the catalytic systems applied for hydrogenation and the formation of the novel carbon-carbon bonds in the reactions of cross-coupling such as Suzuki, Heck, or Sonogashira type. It is generally agreed that independent of which is the particular starting form of the metal, the catalytically active species in majority cases is a Pd(0) cluster or complex. Therefore, a combination of $Pd_2(dba)_3$ and a ligand (for example, a tertiary phosphine) has been often used in catalysis. This is the dissociative mechanism of catalysis involving Pd(II) – Pd(0) system. The associative mechanism based on Pd(II) – Pd(IV) pair was also proposed [14] but less accepted. In many reactions with palladium salts, Pd black is formed that is complex or cluster of Pd(0) or Pd(I). Leonard and Franzen [15] observed the formation of hexagonal microstructures of 1 without admixture of metallic palladium.

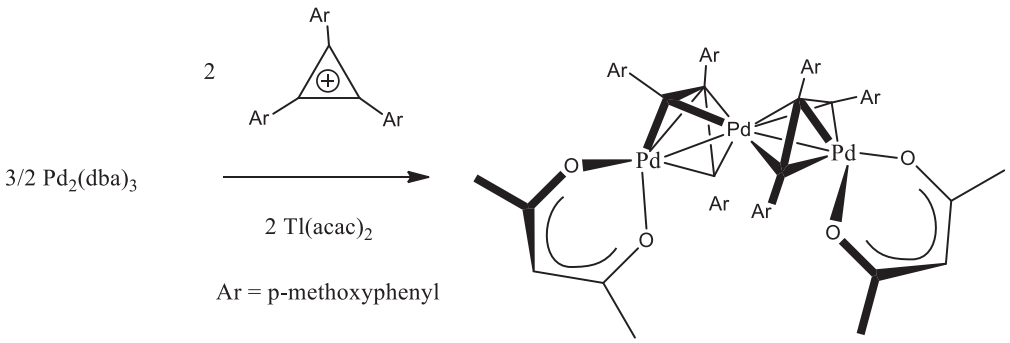
Coordinatively unsaturated, Pd(0) species, can be considered as the electron-rich carbenoids, so they are apt to insert, for example, into some polyfluorinated molecules between two metals [16]. They also were used to build homo- or heterometallic chains. The examples can be found in polymetallic chains and 1 was frequently used for the formation of Pd-to-metal bonds, first for preparing Pd-Pd bonds and chains supported by some ligands.

Palladium is known to build homoatomic bonds. Zerovalent complex 1 appeared to take active part in this process. Reaction of cationic $[PdL_4]^{2+}$ X^{-2} (L = CH_3CN) with 1 (Scheme 2) afforded the dication 2 that appeared to be a suitable reagent for the transfer of the intact Pd-Pd group to some unsaturated molecules.

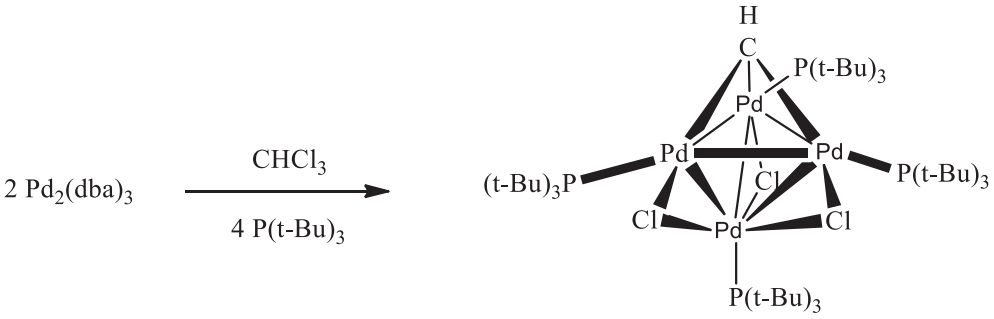


Scheme 2

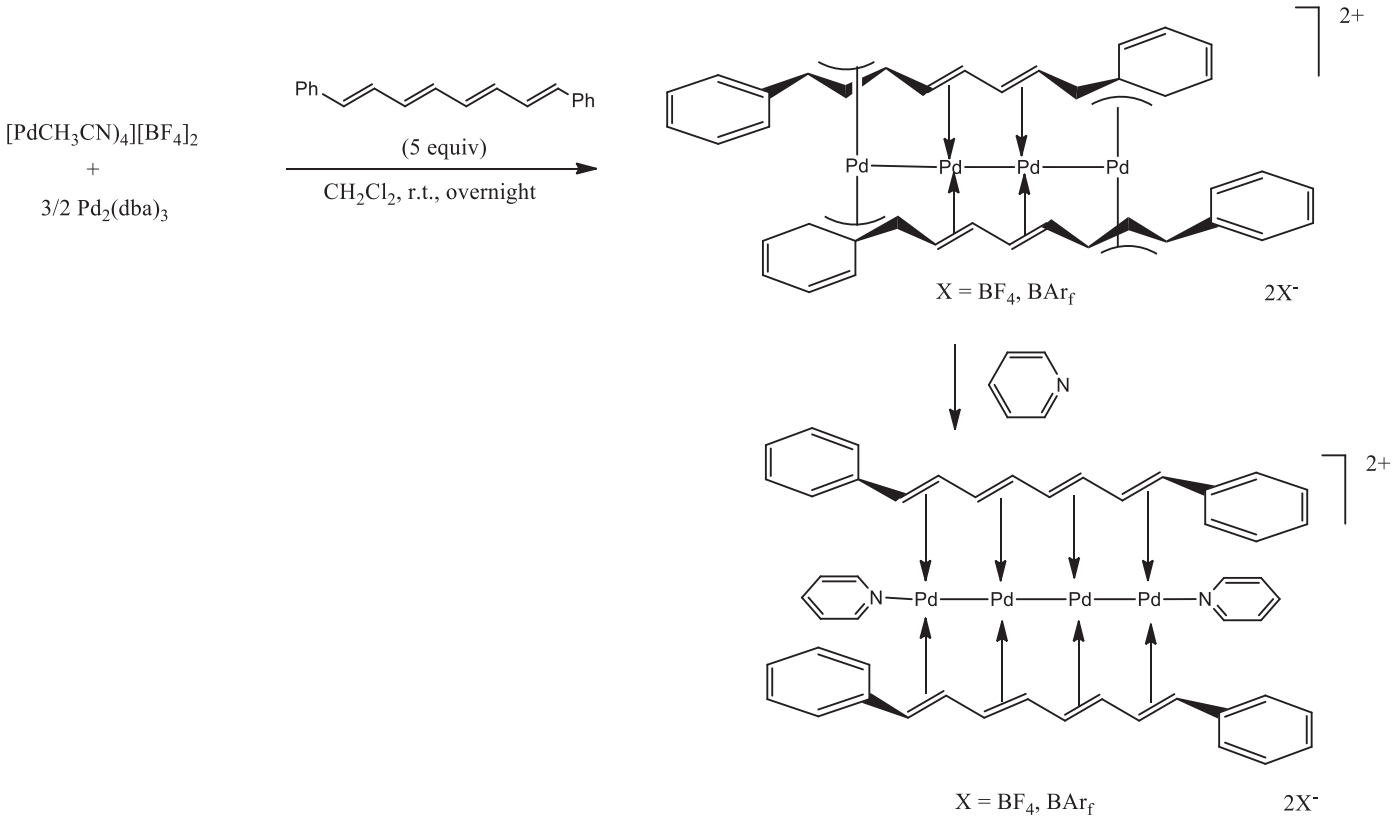
Several interesting examples have been summarized in a review by Murahashi and Kurosawa [17] such as the preparation of the linear Pd_3 bond from triarylcyclopropenium cation [18] (Scheme 3), synthesis of the tetrahedral Pd_4 from chloroform (Scheme 4) in the presence of a tertiary phosphine [19], and the transfer to supporting diarylpolyenes [20] (Scheme 5).



Scheme 3

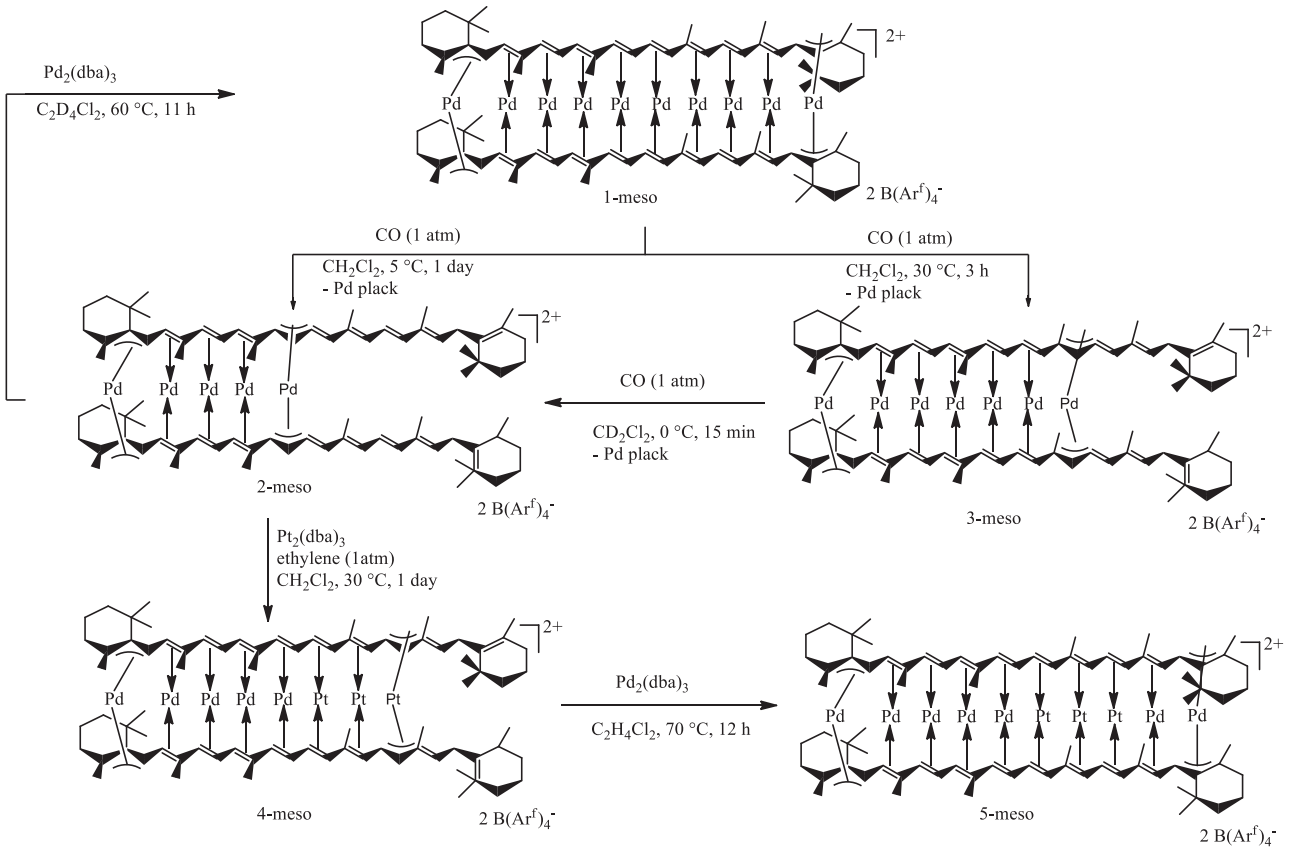


Scheme 4



Scheme 5

Later on, the polyunsaturated chains have been extended as long as 10 metal atoms placed similarly between two parallel carotenoid units but filling, in part, the empty holes with platinum atoms using $Pt_2(dba)_3$ to reach the mixed-metal Pd/Pt carotenoid complex (Scheme 6) [21].



Scheme 6

4. NEW TIMES: $Pd_2(dba)_3$ AS A PRECURSOR OF PALLADIUM (NANO)CLUSTERS

Molecular palladium clusters with ligands R_3P or/and CO, including heterometallic clusters, were the subject of the thorough synthetic and structural investigations. The source of the metal was either Pd(II) acetate or $Pd_2(dba)_3$, see, for example [22]. When fullerenes became available for chemical synthesis, complexes with Pt(0) and Pd(0) having phosphine ligands also were prepared and fully characterized [23, 24]. The direct method for preparing the complexes $(\eta^2\text{-Cn})Pd(L)_2$ with different phosphine ligands was introduced wherein the complex $Pd_2(dba)_3$ provides palladium(0) atom [25].

$$Pd_2(dba)_3 + C_n + 2L \rightarrow (\eta^2\text{-}C_n)Pd(L)_2$$
$$n = 60, 70, L = PR_3 \text{ (R = alkyl, aryl)}$$

However, without support of the other ligands, reaction between fullerene and $Pd_2(dba)_3$ in solution led to the ill-characterized polymeric products with different ratio C_{60} : Pd, all of which exhibit catalytic properties in the hydrogenation of alkenes [26]. Very recently, the direct high temperature synthesis between C_{60} and 1 has been carried out [27] near the melting point of the latter (150°C). The palladium-polymer phase was formed with loss of 1 to give Pd_2C_{60}, an efficient catalyst for the growth of helical carbon nanotubes CNT. This phase easily collapsed under the electron beam into nanoparticles.

The detailed investigation of many samples of $Pd_2(dba)_3$ from different sources, both commercial and laboratory-made, has been performed [28], and it was found in a majority of cases the admixtures of metallic Pd were present, sometimes as high as ~70 %. Besides, the thorough NMR analysis revealed the presence of geometric isomers due to cis-trans isomerism of double bonds. This means that catalytic activity to some extent can be explained by the presence of palladium metal. The purest sample (99%) was obtained from the synthesis performed in $CHCl_3$ with the following crystallization of the solvate from $CHCl_3$ – acetone on cooling. It exhibited high activity in the Heck reaction as expected. So, the preparation in laboratory seems to be preferable.

5. NEW STRAIGHTFORWARD SYNTHESIS OF PALLADIUM CATALYSTS IMMOBILIZED ON CARBON AND NON-CARBON POLYMERIC SUBSTRATES

After fullerenes carbon nanotubes (CNT) became known, it was clear that a whole family of nanocarbons does exist including nanodiamonds, graphenes etc. [29].

One important feature which fullerenes and nanotubes have in common is the presence of strained double bonds. The character of distortion is similar, that is C-C bonds are bent in the same fashion, in out-of-plane direction. Comparison between both species, fullerenes and carbon nanotubes (CNT), is presented in Table 1 [30].

One of the first experimental evidences for their similarity has been found during the EPR study of free radical addition on the strained double bonds [31]. The corresponding data are shown in the Table 2.

We used the above-mentioned similarity as a starting point for the direct synthesis of the novel efficient palladium(0) nanocatalyst Pdx/CNT using synthon 1 [32]. The first equivalent of 1 gives supposedly the π-complex with one strained double bond of a CNT. If no other ligands are present, the free valence of

Table 1. Similarity and difference between fullerenes and carbon nanotubes

Fullerenes	**Carbon Nanotubes**
Individual molecules	Polymeric
Limited solubility	Insoluble *per se*
Double bonds are strained	**Double bonds are strained**
Inner cavity is ellipsoidal	Inner cavity is cylindrical or conical
Capable of irreversible introduction of atoms and small molecules into the inner cavity	Capable of reversible introduction of atoms and small molecules into the inner cavity

Table 2. Comparison of the ESR data for chromium and molybdenumradical-adducts of fullerenes and carbon nanotubes. T = 295 K.

	"Cr"		"Mo"	
	g-factor	a(53Cr), G	g-factor	a(95Mo), G
C_{60}	2.0134	13.25	2.029	18.8
C_{70}	2.0138	13.25	2.029	18.8
CWNT	1.9929	16.5	2.0008	33.0
	1.9938	15.0	2.0148	38.0
			1.9750	*

this first palladium atom is saturated by the other equivalents of Pd(0) until this is still advantageous in terms of energy. Size of nanoclusters is determined by the balance of the outer and inner metal atoms. Isolated metal nanoclusters are formed along the length of CNT, they play a role of the catalytic centers.

CNTs were prepared by pyrolysis of methane in the presence of hydrogen on the catalyst of the composition $(Co_3Mo_1)_{0.02}Mg_{0.98}O$ at 950°C [33].

According to transmission electron microscopy (TEM) data (JEOL JEM-100C, accelerating voltage 100 kV), the product is indeed a CNT with a diameter of 3–6 nm, with two to three layers; therefore, following the accepted classifications, they should be related to multiwall CNTs (Fig. 2), CNTs thus obtained without any additional treatment were used as substrates for the deposition of palladium by reacting with **1** [32].

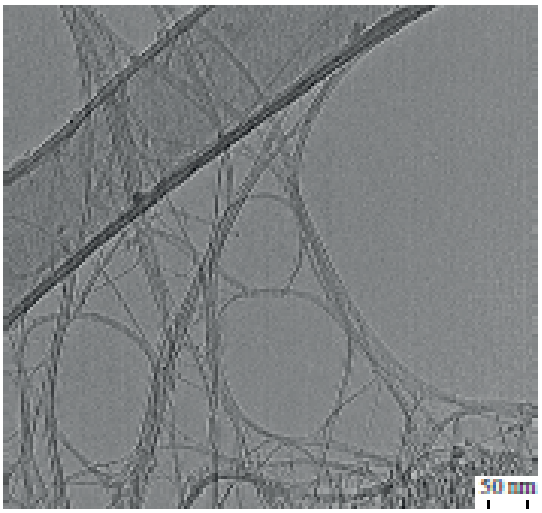


Fig. 2. TEM image of initial CNT

The resulted Pd catalyst was prepared from the wine-red solution of 1 in toluene and magnetically stirred slurry of CNT under argon at 50 °C. In the course of quick reaction, color of solution turned to straw-yellow typical of free dba. After washing and drying the catalyst contained 6% of palladium. In the micrograph obtained (Fig. 3), black dots of palladium nanoparticles are clearly seen on the gray backgrounds of carbon nanotubes.

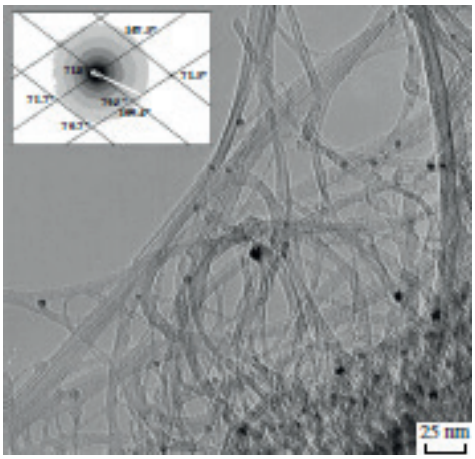


Fig. 3. TEM image of CNT with deposited Pd particles; in the insert: microdiffraction of Pd particles.

The TEM measurement of sizes of Pd nanoparticles gives the distribution of a rather narrow range: from 2.5 to 6 nm (Fig. 4). From microdiffraction data it is also possible to conclude that metallic palladium crystallizes in a face-centered cubic lattice, which corresponds to the reference data for palladium. Palladium particles formed mostly single crystals.

This nanocatalyst Pdx/CNT appeared to be an efficient catalyst for the following cross-coupling such as Heck, Suzuki, and Sonogashira reactions as shown on Scheme 7 [32].

The direct addition of Pd_2dba_3 to hydroxy-SWNT (SWNT – single-wall nanotubes) modified by acylation with optically active natural α-amino acids resulted in the nanopalladium SWNT (Scheme 8) used as active catalysts of the hydrogenation of the unsaturated substrates some of which were prochiral giving after reaction the products with a chiral carbon bearing CH_3 group at tertiary atom (Table. 3). In the case of hydroarylation of norbornene they also exhibit high catalytic activity (65-100 %). However, no asymmetric reaction was observed, probably because of the large distance between the catalytic and asymmetric centers in the catalyst [34, 35].

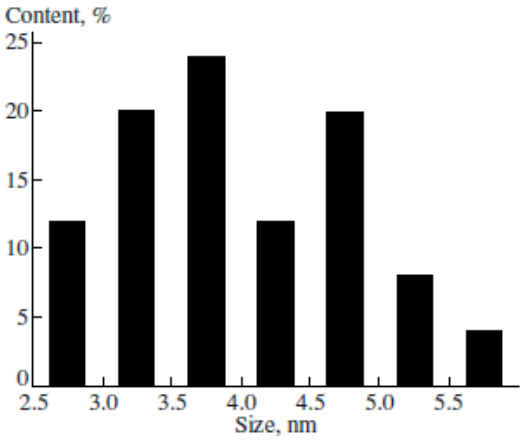
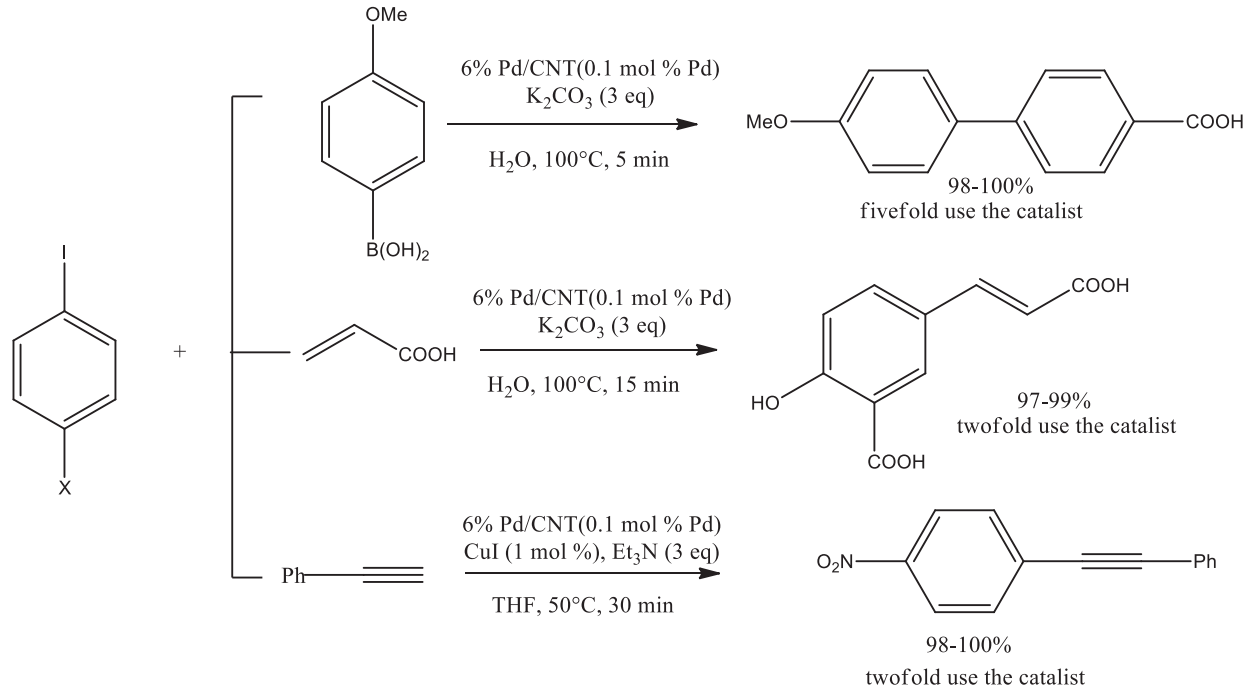
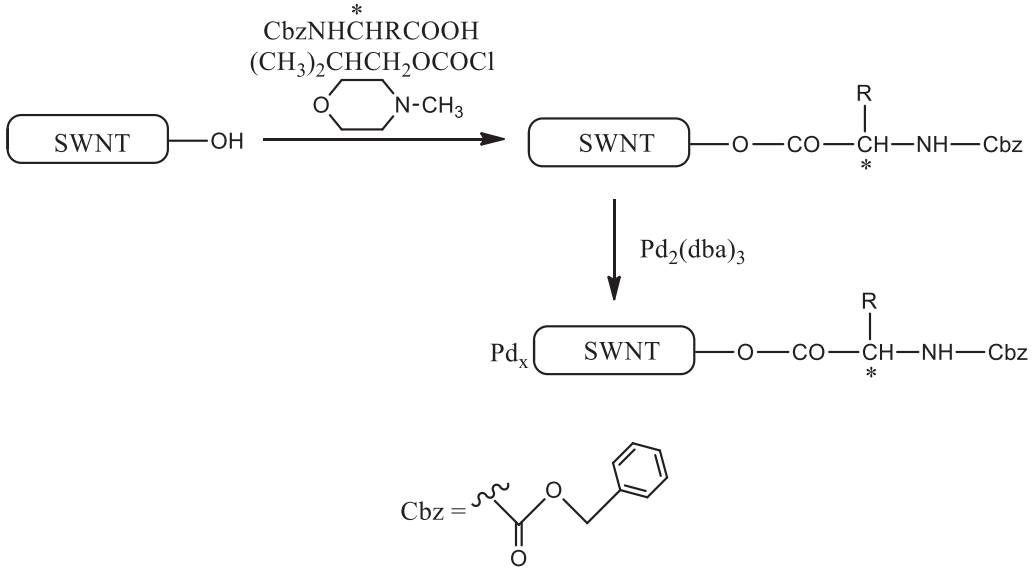


Fig. 4. Size distribution of Pd particles immobilized onCNT according to TEM data (plotted by measuring 25 particles).



Scheme 7



Scheme 8

Table 3. Hydrogenation of α-acetamidostyrene and α-phenylcinnamic acid on the palladium catalysts prepared from hydroxyl-CNT acylated with an enantiomeric α-amino acids[a]

Entry	Catalyst	Substract (S)	S/Cat[b] (nol/g-atom)	MeOH ml	Conversion (%)
1	3% Pd-CNT-L-valine[c]	$PhC(NHAc)=CH_2$	1000	3	92
2	3% Pd-CNT-L-valine[c]	$PhC(NHAc)=CH_2$	200	2	100
3	3% Pd-CNT-L-valine[c]	PhCH=C(Ph)COOH	200	2	71
4	6% Pd-CNT-L-methionine[d]	$PhC(NHAc)=CH_2$	200	2	65
5	6.7% Pd –CNT-L-proline[d]	$PhC(NHAc)=CH_2$	200	2	100
6	6.7% Pd –CNT-L-proline[d]	PhCH=C(Ph)COOH	200	2	68

[a] The hydrogenation conditions: $p(H_2)$ = 19 atm, 60 °C, 5 h.
[b] The substrat/catalyst ratio.
[c] The amount of catalyst is 4 mg.
[d] The amount of catalyst is 2 mg.

Mechanism of binding Pd(0) by nanodiamonds and graphenes is obviously different since they do not have any strained double bonds. Nonetheless, the addition of $Pd_2(dba)_3$ occurs with the formation of catalytically active palladium species (Fig. 5) [36, 37].

It seems that the metal is bound at the outer shell of the carbon nanoparticles. Moreover, this approach was proved to work outside the limits of carbon chemistry. It was successfully used for introducing palladium into the inorganic double-layered complexes with a magnetite nucleus to give a superparamagnetic Pd-catalyst (Fig. 6) [38].

Another example of introducing Pd(0) by way of 1 to the inorganic nanotubes based on WS_2 fragments (Fig. 7) has demonstrated universal application of this method in preparation of the active catalysts of cross-coupling [39].

Catalytic properties of Pd/DND have been studied on the example of hydrogenation reactions of double and triple bonds. As reactants were used diphenylacetylene, α-phenylcinnamic acid and unsaturated enamides. The degree of conversion was about 100 %. The catalytic activity of other Pd-contained nanoparticals in cross-coupling reactions is summarized in the table 4.

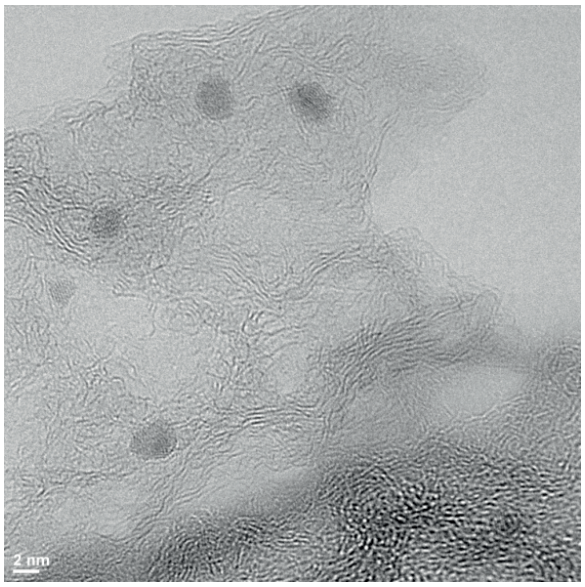


Fig. 5. High resolution TEM images of Pd particles on the graphene shells that have been used for estimation of interplanar spacing.

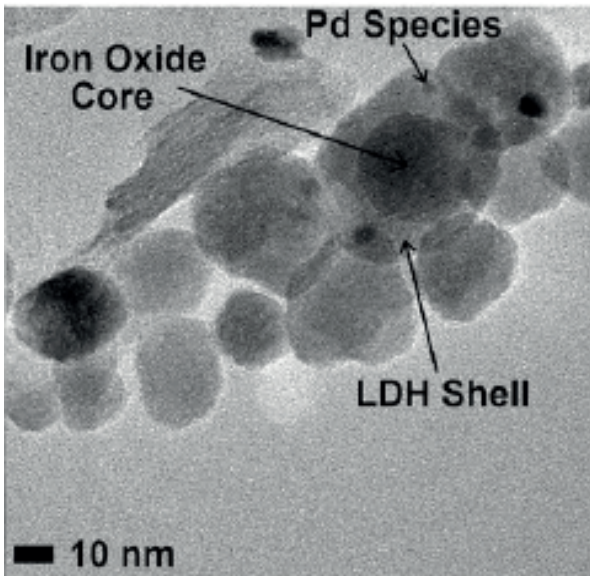


Fig. 6. High magnification TEM image of the palladated catalyst (LDH - layered double hydroxides).

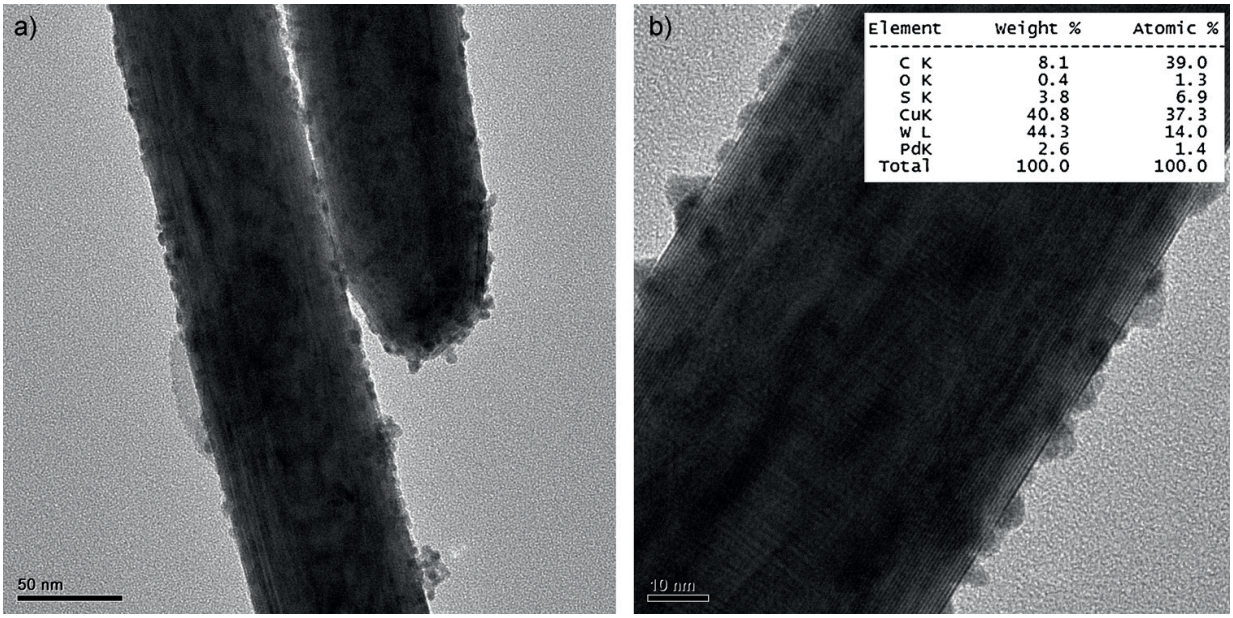


Fig. 7. TEM images of a) individual decorated nanotubes demonstrating uniform surface coverage and b) a closer look at a decorated nanotube, showing WS2 layers, with the corresponding EDS analysis (inset).

Fig. 7. Catalytic activity of Pd-nanoparticals in the cross-coupling reactions/

Catalyst	Suzuki reaction Yield, %	Heck reaction Yield, %	Reference
Pd/graphene	90	100	36
Pd-LDH@M	78	100	37
$[(WS_2)_5Pd_1]_m$	86	91	38

6. CONCLUSIONS

The main interest of the above-described field is concentrated on the versatile synthesis and application of the heterogeneous palladium catalysts in the organic reactions (for a review, see [40]) under the conditions required by green chemistry. Other applications of the Pd(0) complex are less studied, such as the noticeable anticancer activity of **1** found *in vivo* [41]. Palladium (0) complexes with some analogs of dba, electrochemically active, have been also synthesized [42, 43].

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